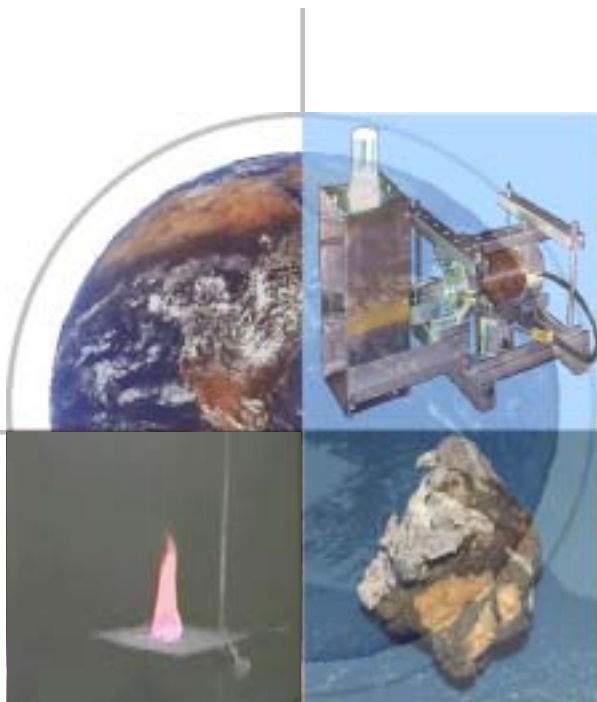# ENHANCEMENT IN THE STORAGE OF METHANE IN HYDRATES

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Advanced Fuels Systems Focus Area
National Energy Technology Laboratory

Dirk D. Link, Edward P. Ladner,
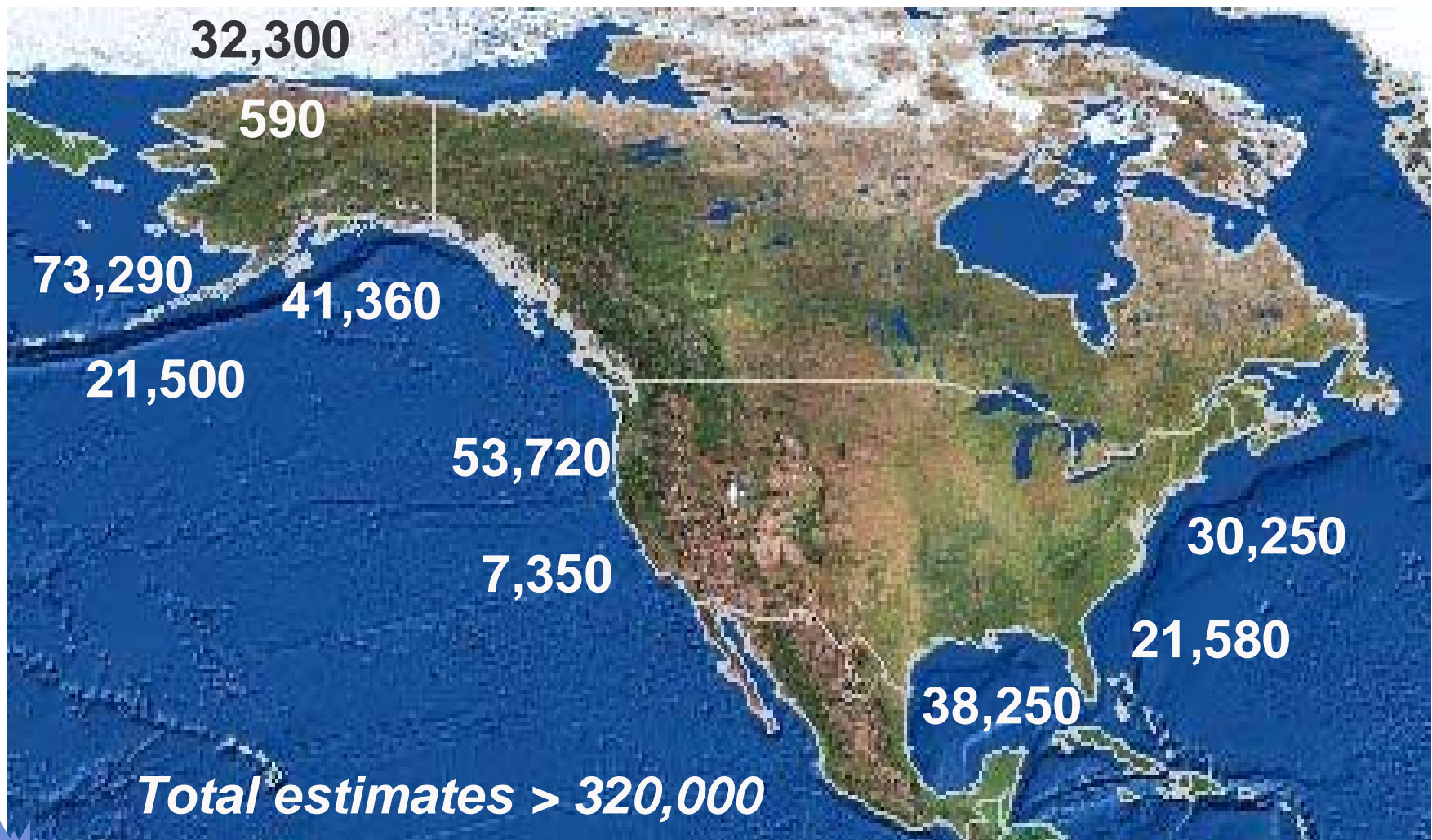**and Heather A. Elsen**

Outline

- **Methane Hydrates Overview**
  - Supply, location, etc.
  - Energy storage applications

- **Problem/Difficulty to be Addressed**
  - Natural hydrate systems do not approach theoretical maximum uptake of methane

- **Enhancing Storage**
  - Identify optimum formation parameters
  - Examine effectiveness of surfactant addition to form hydrates

- **Results Summary**
  - Experimental parameters
  - Optimum surfactant thus far

- **Future work**

USGS Estimates of U.S. In-place Methane Contained within Gas Hydrates (Tcf)

32,300

590

73,290

41,360

21,500

53,720

30,250

7,350

21,580

38,250

Total estimates > 320,000

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Methane Storage as Methane Hydrate

- **Advantages**
  - Relatively simple engineering set-up
  - Storage under mild conditions (compared to LNG)
  - Safe, slow release of methane under conditions of failure

- **Applications**
  - Storage at remote locations
  - Transportation of stranded gas to markets
  - Trans-oceanic transport to remote locations (gas and water)
  - Competitive technology for small-scale stranded gas sources

- **Issues**
  - Maximizing amount of methane in hydrate

Storage of Methane in Hydrates Background

- **Previous research focused on the conversion of methane to methanol**

- **Preliminary experiments revealed high conversion of methane is possible**
  - Solubility of methane was limiting

- **During the course of conversion studies, methane hydrate formation explored to maximize methane conversion**
  - Reaction conditions
  - Physical mixing
  - Additives

- **Interested in maximizing storage of methane**

Preliminary Studies on Hydrate Formation

- **Typical time versus temperature and pressure profiles**
  - Binary (methane-pure water) system
  - Simulated seawater

- **Evaluation of stirring**

- **Pressure conditions**
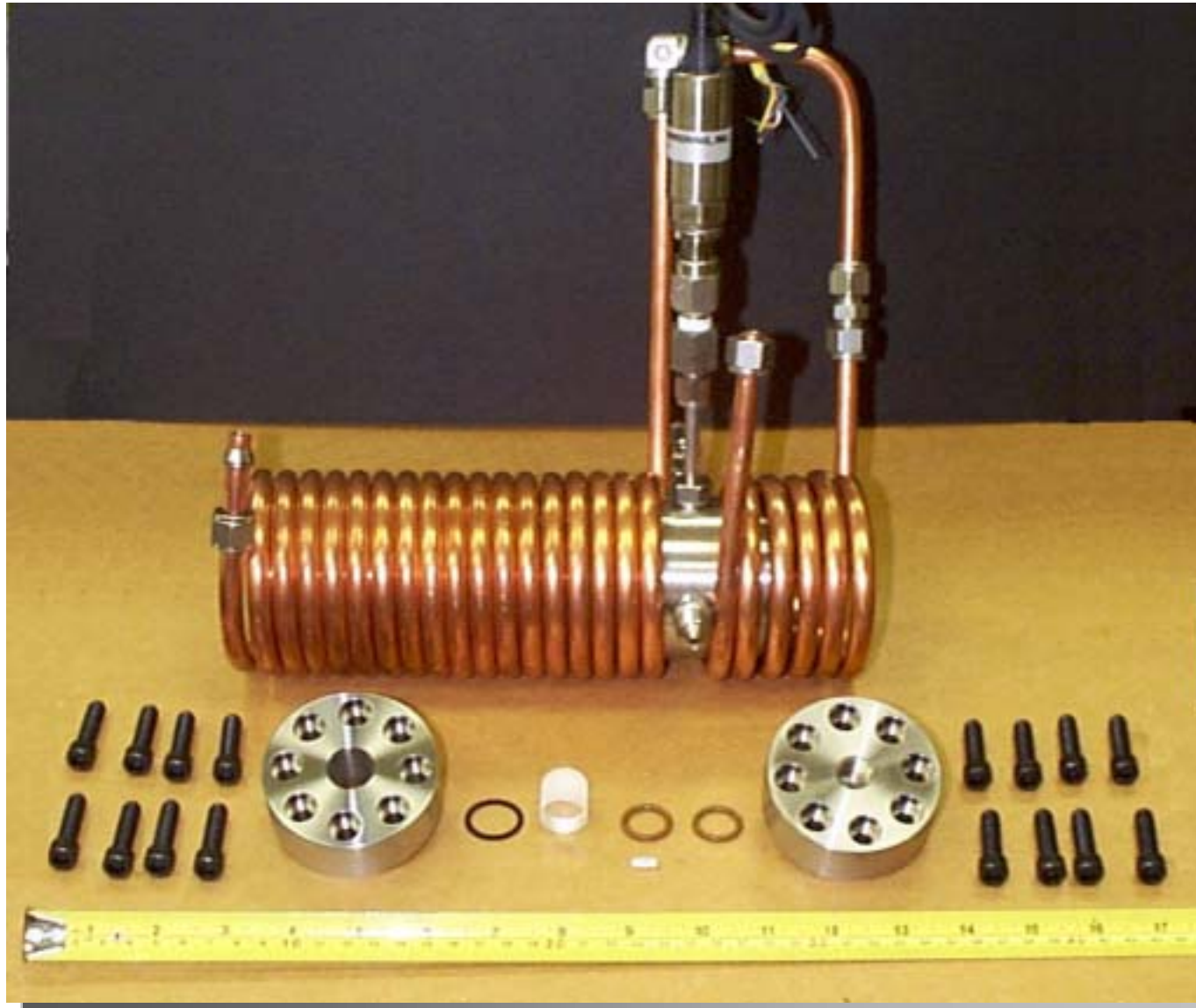
- **Hysteresis Effect**

Experimental Details

- **High-pressure cell filled with volume of chosen reactant**
  - Pure water
  - Simulated seawater (3.2% net NaCl and $MgCl_2$)

- **Headspace filled with 99.999% methane**
  - Static pressure at ~1400 psig initial
  - Constant pressure continuously delivered at ~1400 psig

- **Temperature lowered to form hydrate**
  - Steep pressure decrease signals hydrate formation
  - View cell & CCD camera used to visually observe formation

- **Headspace gas vented at lower temperature**

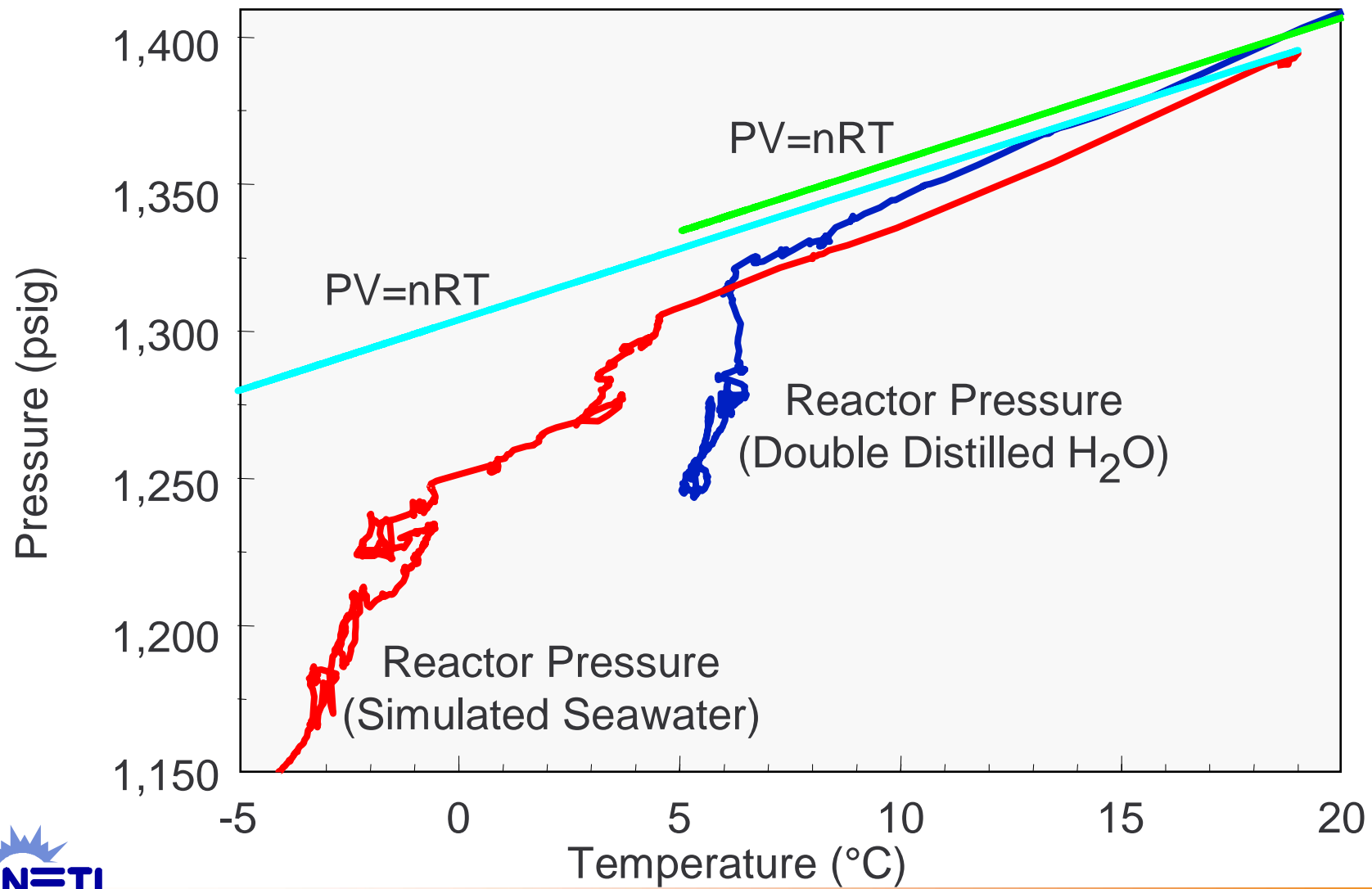- **Cell warmed to dissociate hydrate and evaluate uptake of methane**
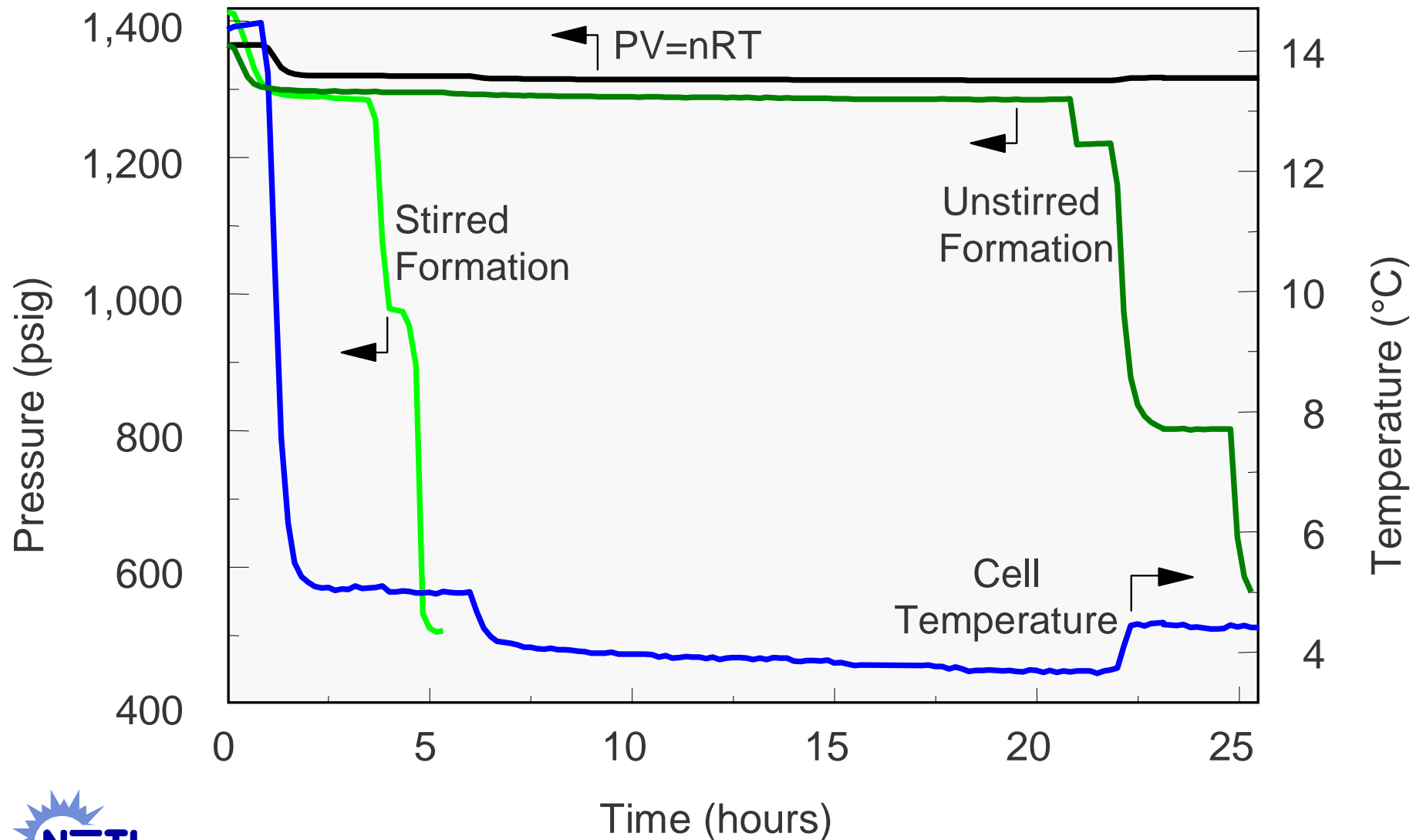
High-pressure View Cell Schematic
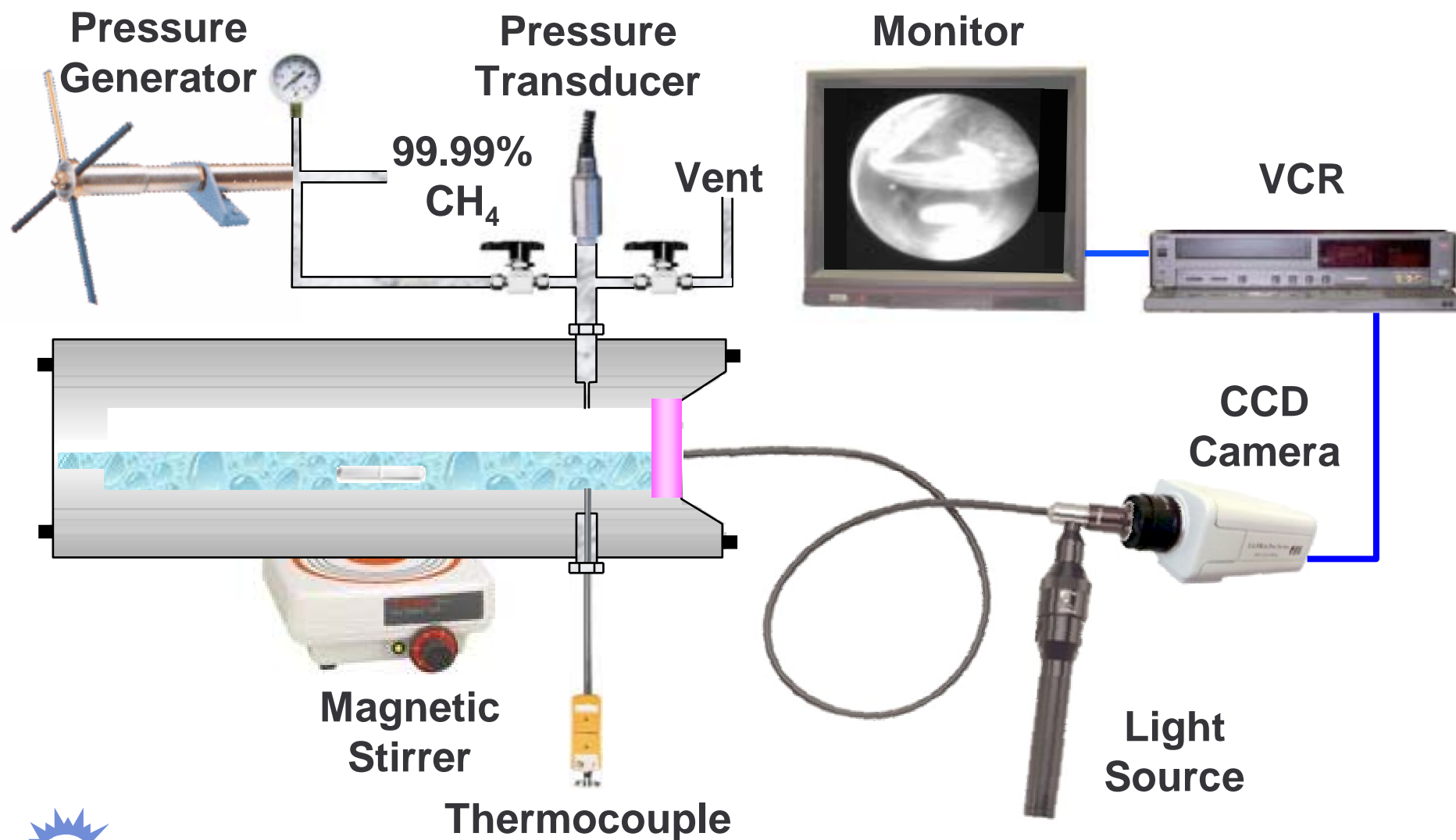
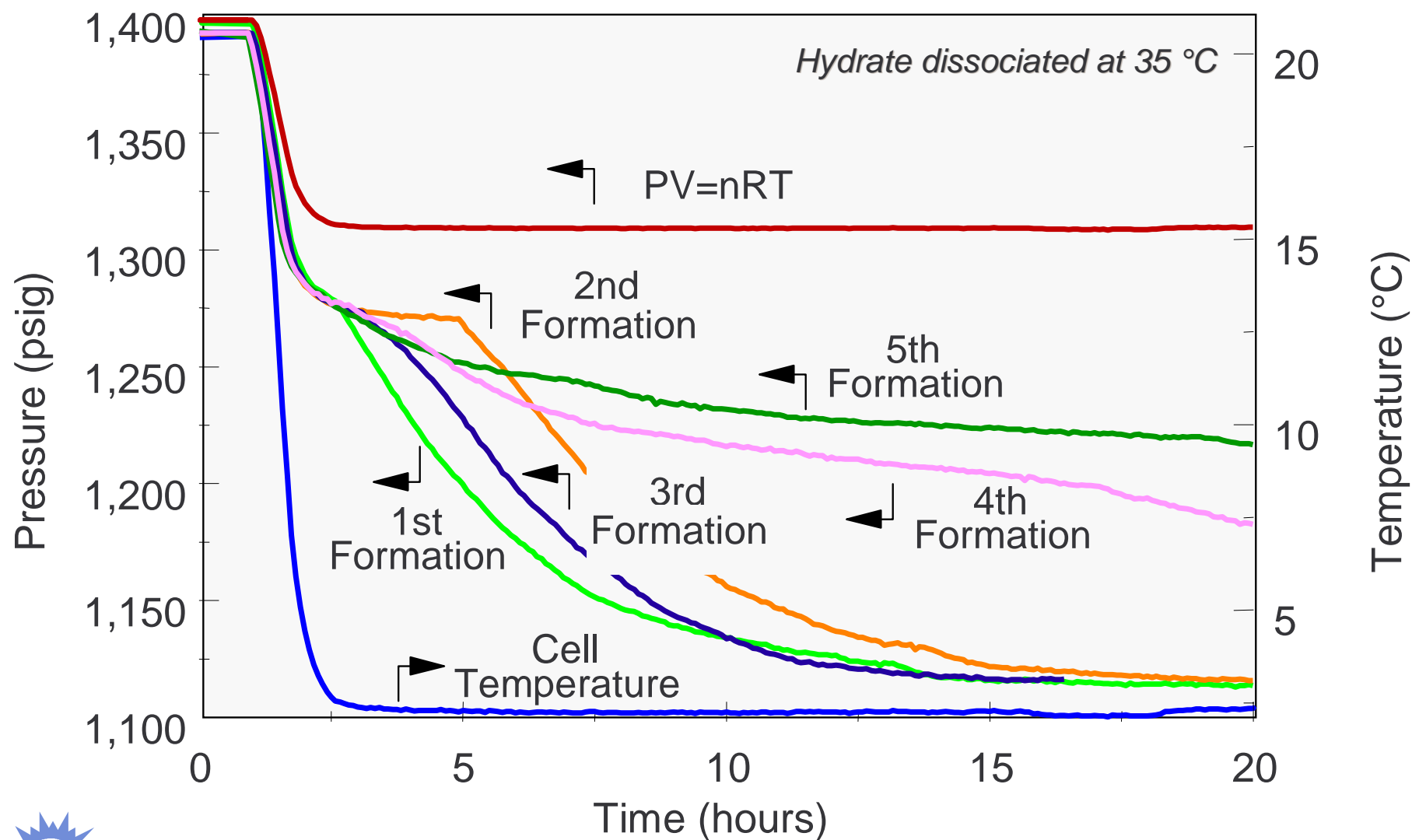# High-pressure View Cell Exploded View

Pressure-temperature Profile Of Hydrate Formation

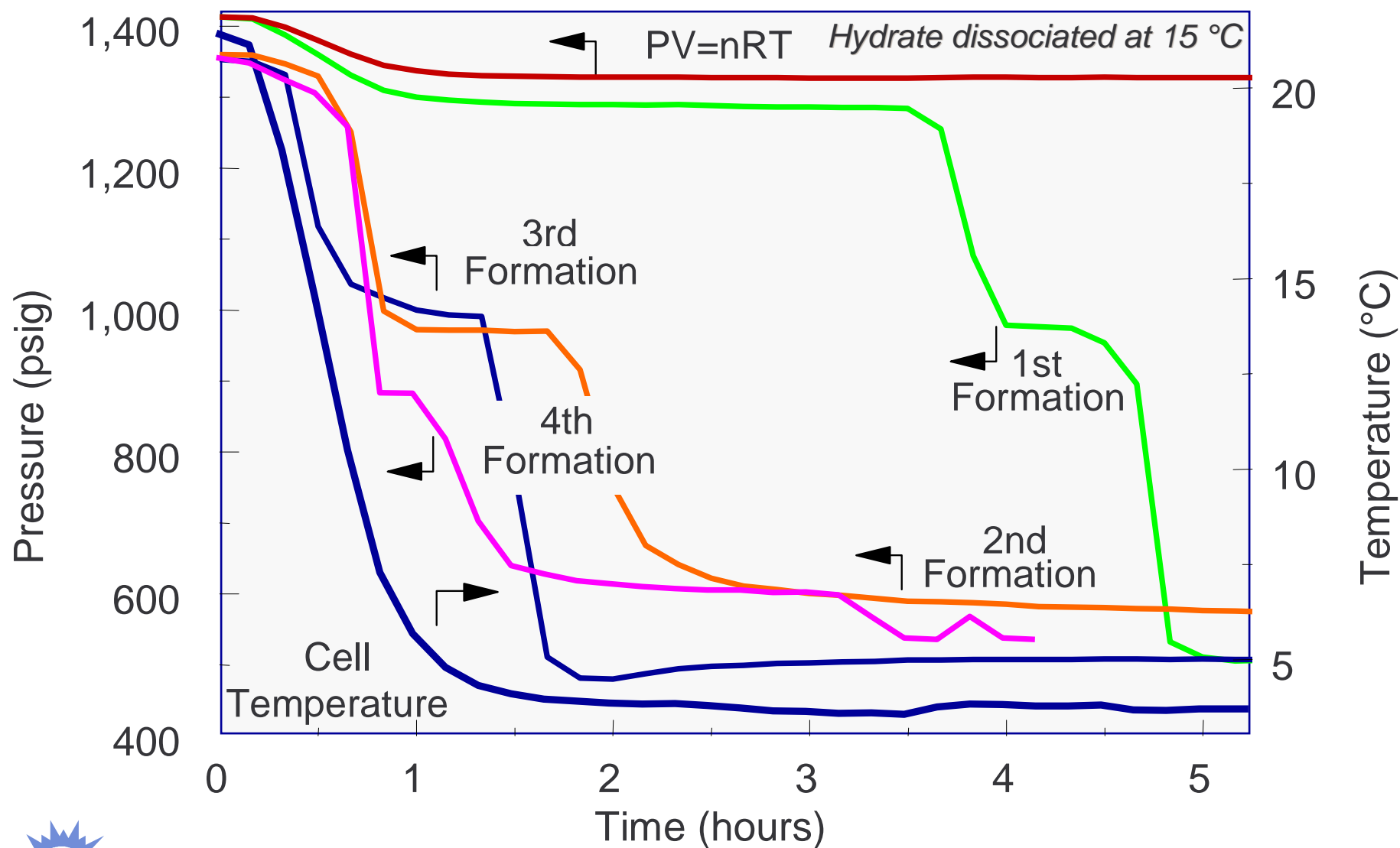Pressure (psig) vs. Temperature (°C)

PV=nRT

PV=nRT

Reactor Pressure
(Double Distilled H_2O)

Reactor Pressure
(Simulated Seawater)

Effect of Stirring on Hydrate Formation

Hysteresis Effect During Hydrate Formations

Hydrate dissociated at 35 °C

PV=nRT

2nd Formation

5th Formation

1st Formation

3rd Formation

4th Formation

Cell Temperature

Pressure (psig)

Temperature (°C)

Time (hours)

Hysteresis Effect During Hydrate Formations

PV=nRT   *Hydrate dissociated at 15 °C*

3rd
Formation

1st
Formation

4th
Formation

2nd
Formation

Cell
Temperature

Pressure (psig): 400, 600, 800, 1,000, 1,200, 1,400

Time (hours): 0, 1, 2, 3, 4, 5
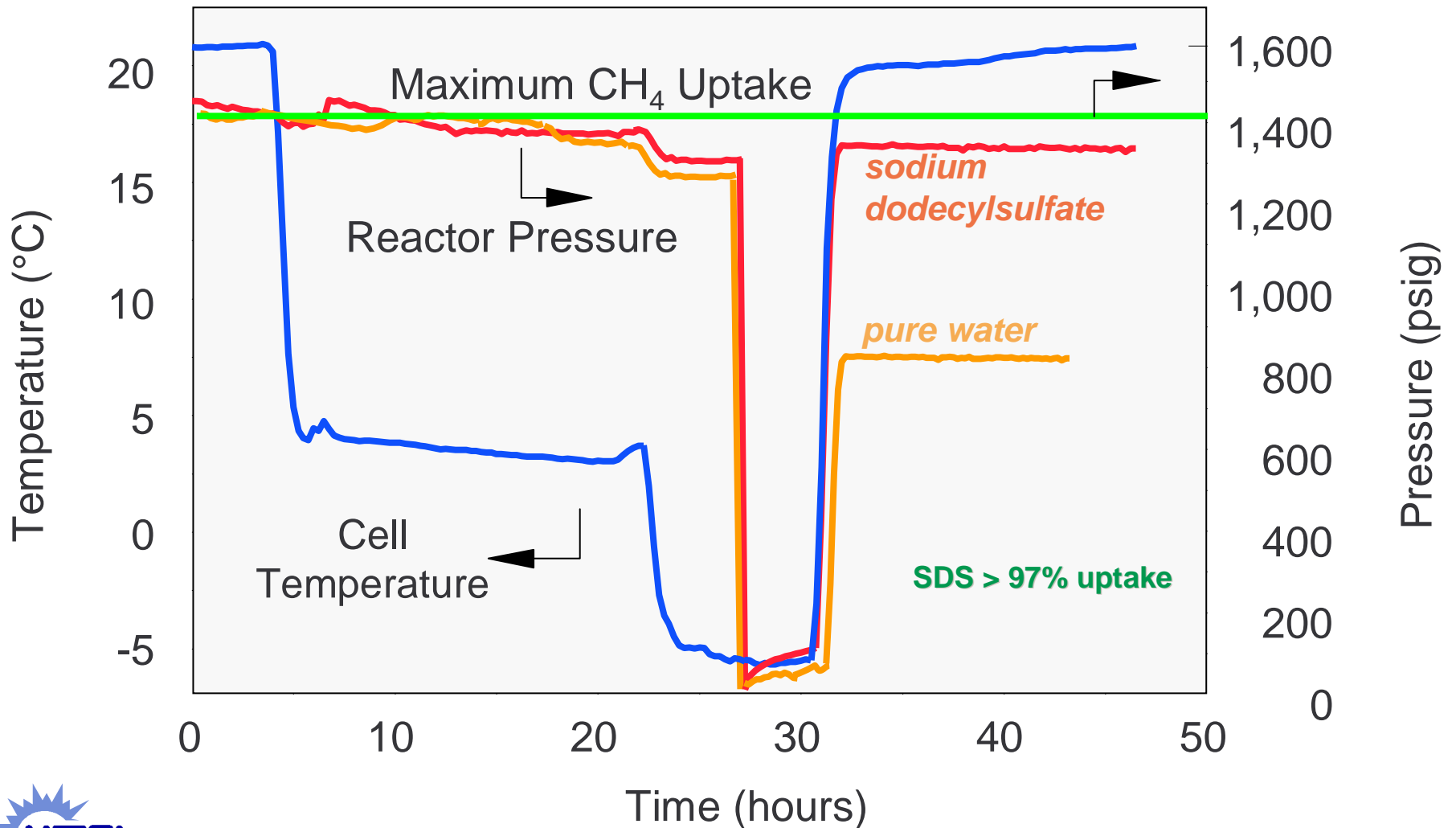
Temperature (°C): 5, 10, 15, 20

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Hydrate Formation With Surfactant Added Under Static Headspace Pressure

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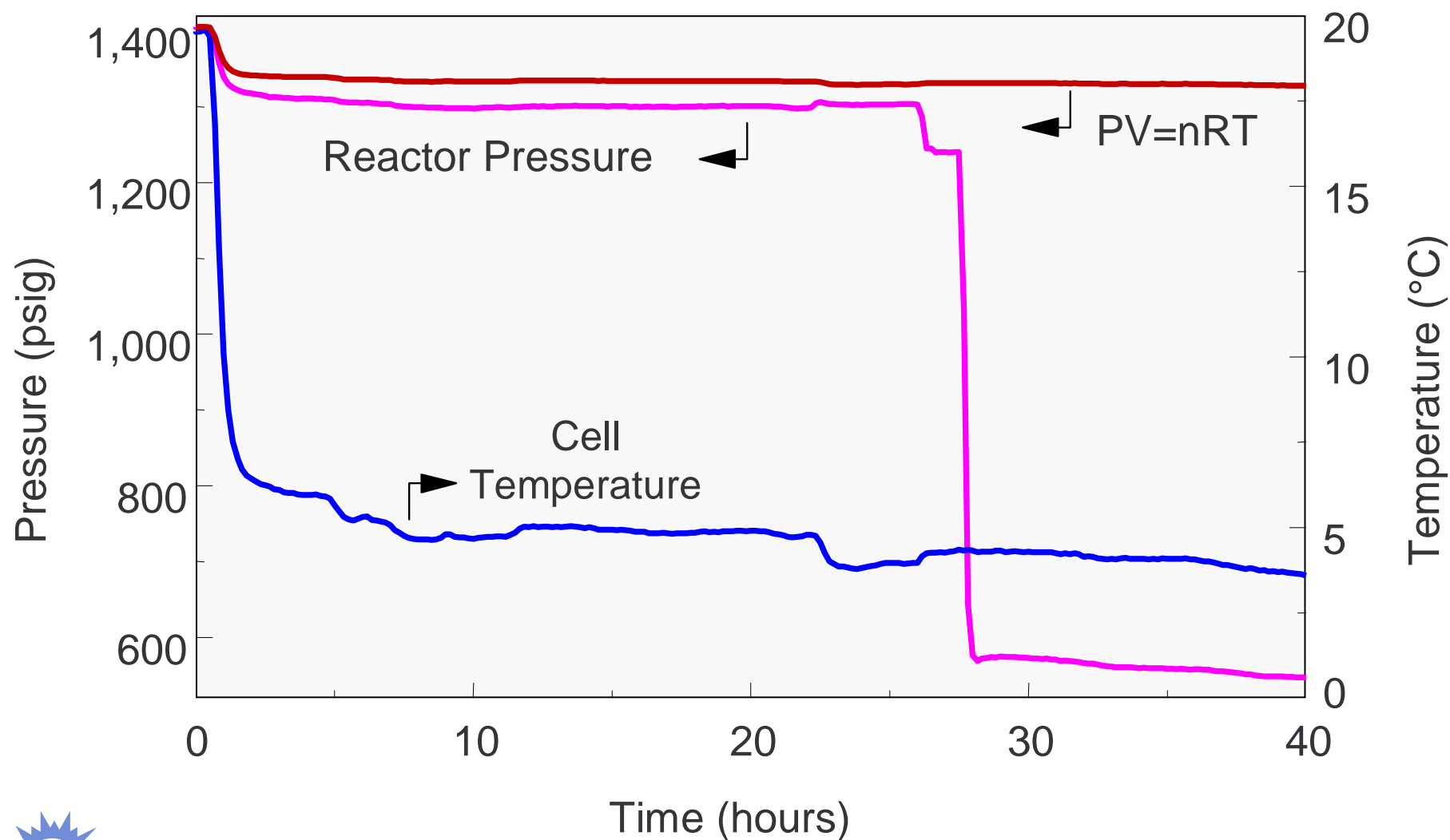
Hydrate Formation Comparison
Under Static Headspace
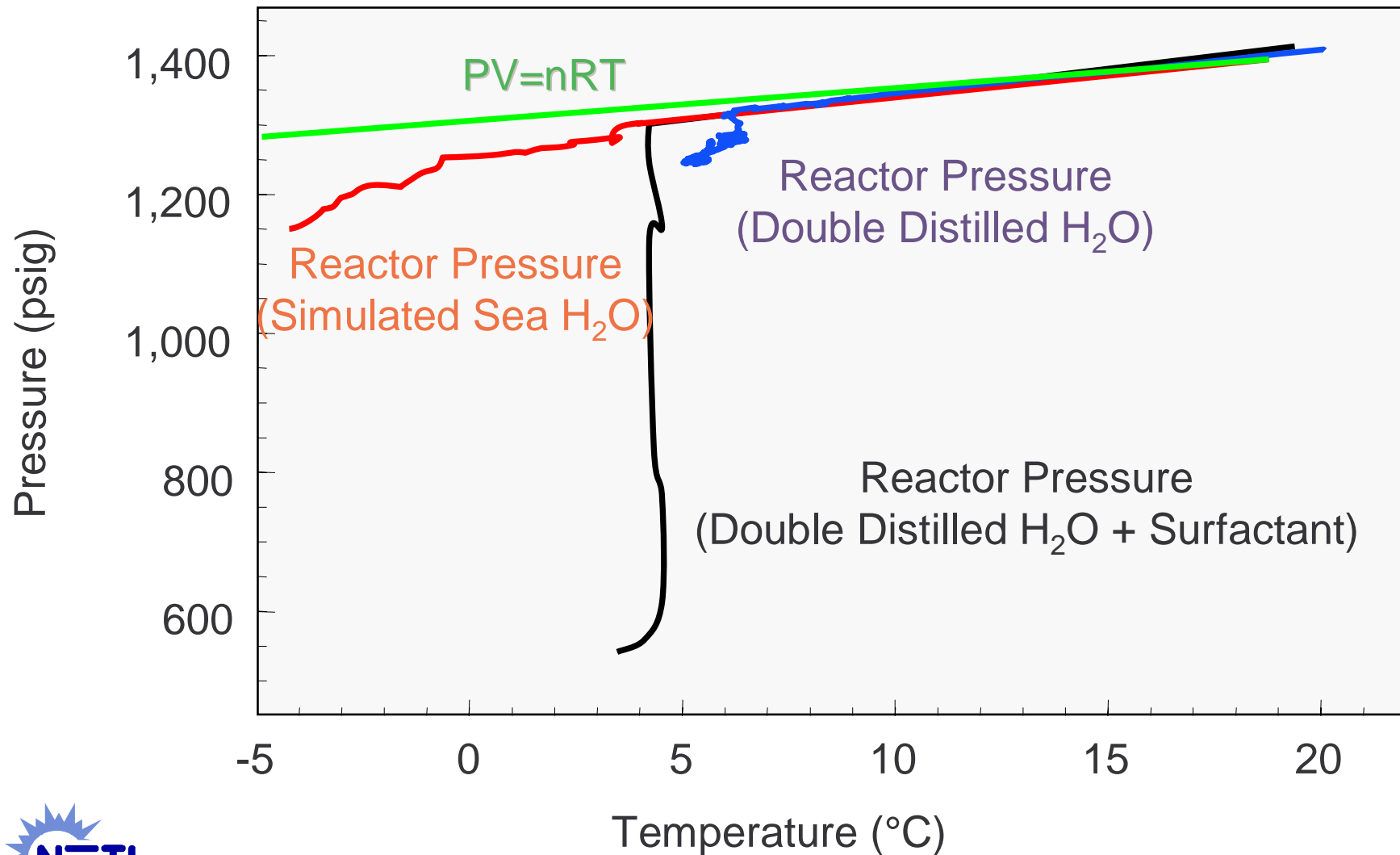
Hydrate Formation Comparison Under Constant Methane Pressure

SDS > 97% uptake

Methane Storage in Sodium Dodecylsulfate System

Constant Head Pressure	Vent Temperature (°C)	Volume Liquid	% CH_4 Uptake
No	-4.5	10	90.75
Yes	-5.5	15	97.26

- **Experimental details for optimization of methane uptake during hydrate formation**
  - Continuous stirring
  - Constant methane headspace pressure

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Additional Surfactants Tested for Storage

Surfactant	Vent Temperature (°C)	Volume Liquid	% CH_4 Uptake
Sodium Dodecylsulfate	-5.5	15	97.26
Dodecylamine	-10.8	10	9.91
Dodecyl Trimethyl Ammonium Chloride	-15.5	10	13.92
Sodium Lauric Acid	-15.2	10	39.54
Sodium Lauric Acid	-16.1	10	77.35
Sodium Oleate	-13.7	10	70.47
Superfloc 16	-14.0	10	19.59
Superfloc 84	-15.1	10	20.05

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Commercial Surfactant Test

Cycle Number	Vent Temperature (°C)	Volume Liquid	% CH_4 Uptake
First	-17.9	10	14.51
Second	-15.1	10	99.10
Third	-19.9	10	16.47
Fourth	-17.3	10	14.76
Fifth	-19.9	10	21.47
Sixth	-19.4	10	54.35

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Kinetics of Hydrate Formation/Dissociation

- **Dr. Faruk Civan and Dr. Richard G. Hughes Mewbourne School of Petroleum and Geological Engineering, University of Oklahoma**

- **Kinetic modeling of hydrate formation & dissociation using NETL data**
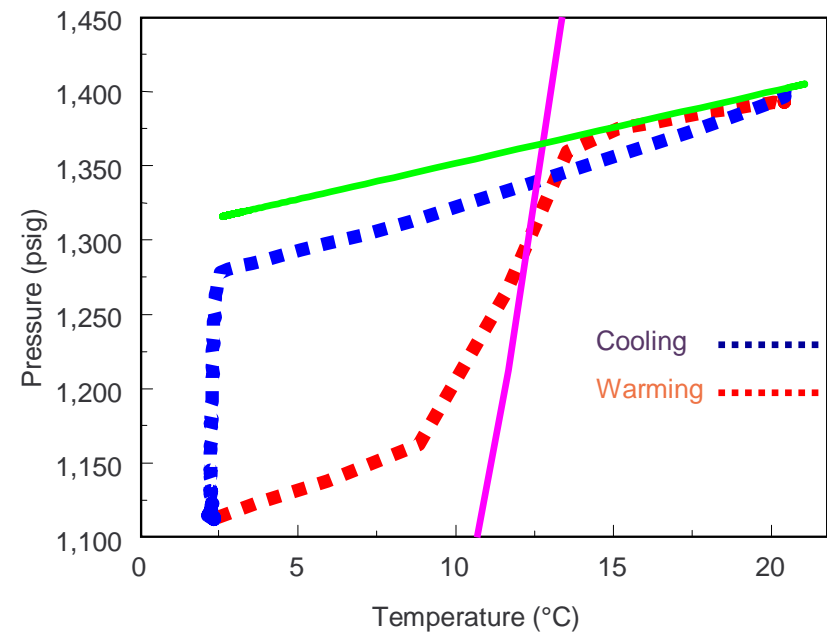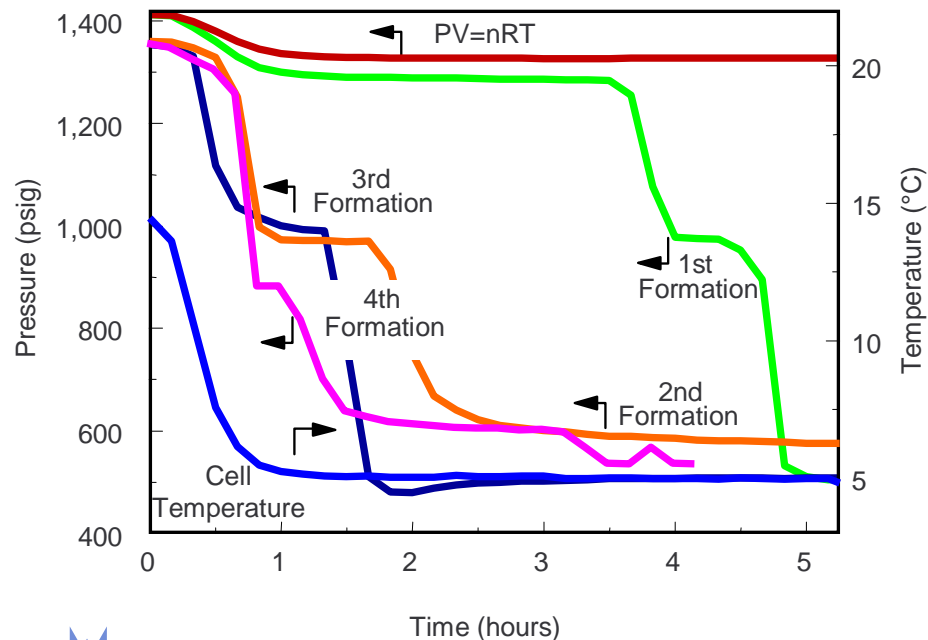
Future Plans and Recent Experimental Work

- **Continuation of surfactant screening study**
  - Examine effects of different types on uptake
    - Anionic and cationic
    - Nonionic
    - Amphoteric
- **Form methane hydrates on larger scale**
  - Explore formation/dissociation characteristics on 30x larger scale (up to 12.2 L cell volume)
  - Expand formation to include "natural" conditions
  - Scale-up of methane hydrate storage
  - Use ultrasonic technique to monitor hydrate formation
- **Use Raman Spectroscopy to evaluate formation of methane hydrates**
  - Initial tests with binary (water-CH_4) system
  - Progress to surfactant systems
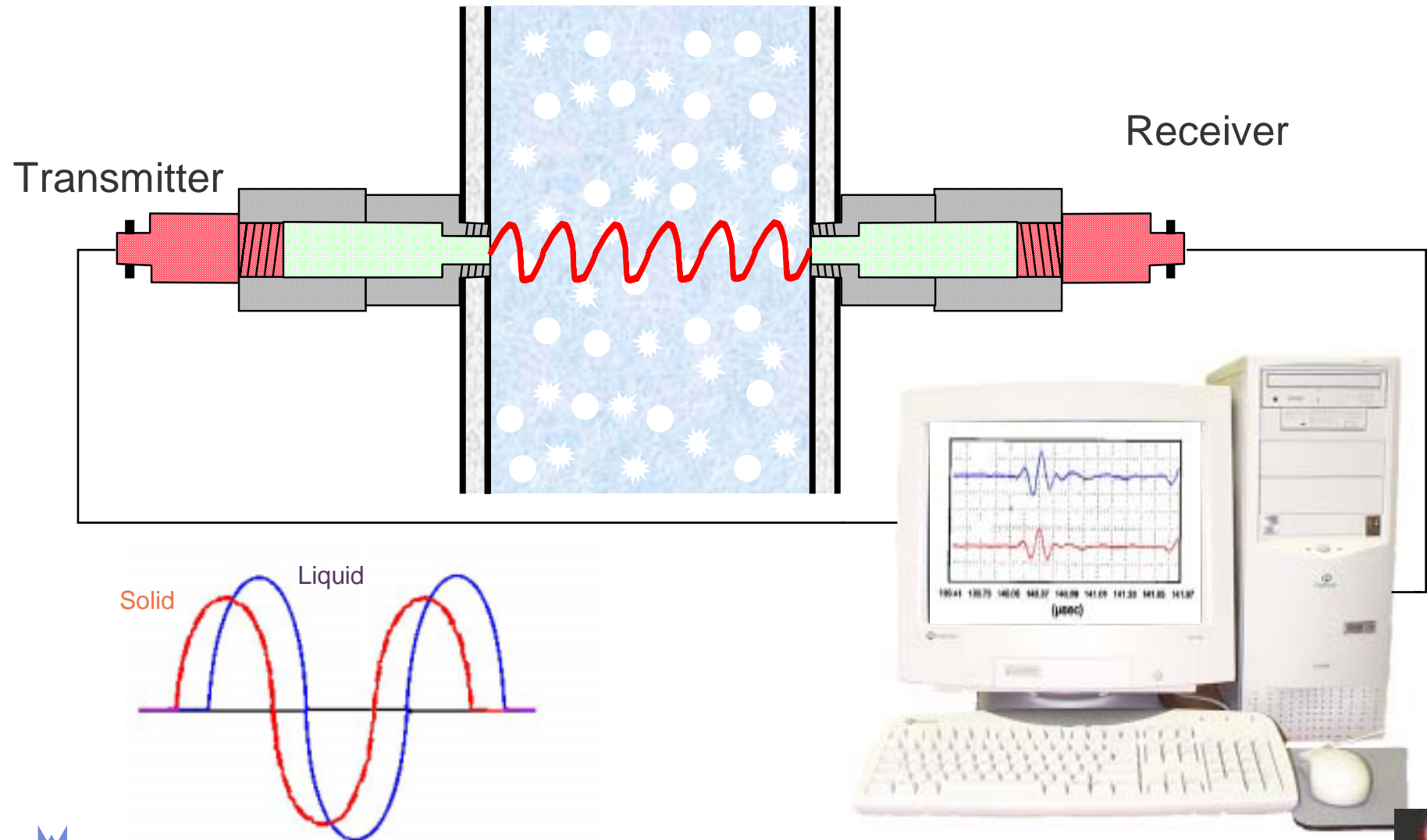 - Real time monitoring of formation?

New Hydrate Facility

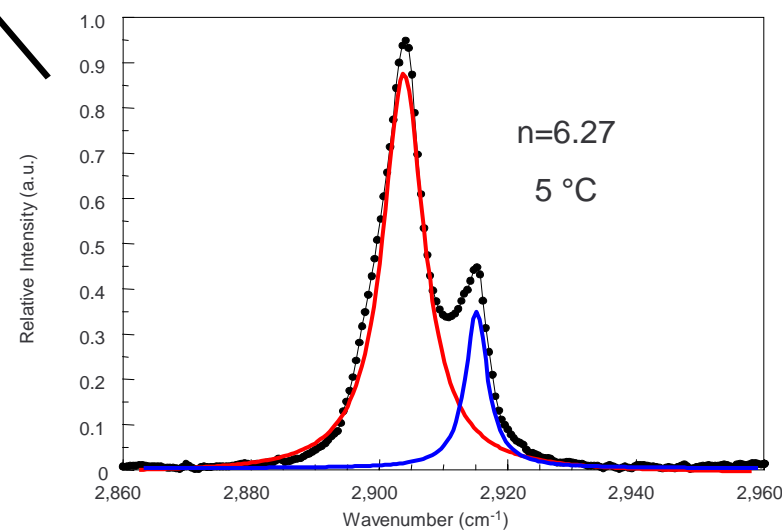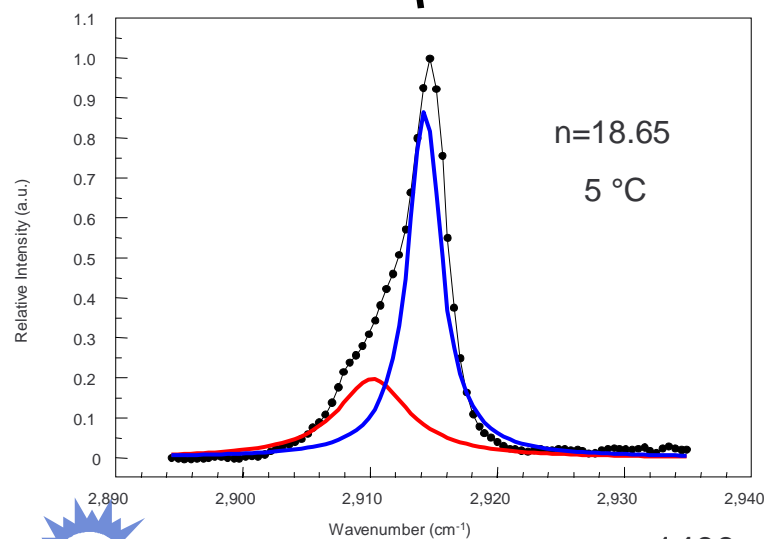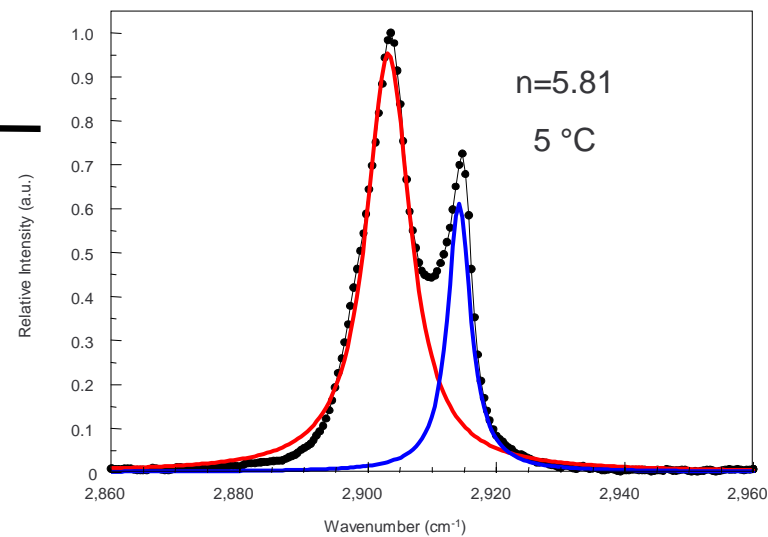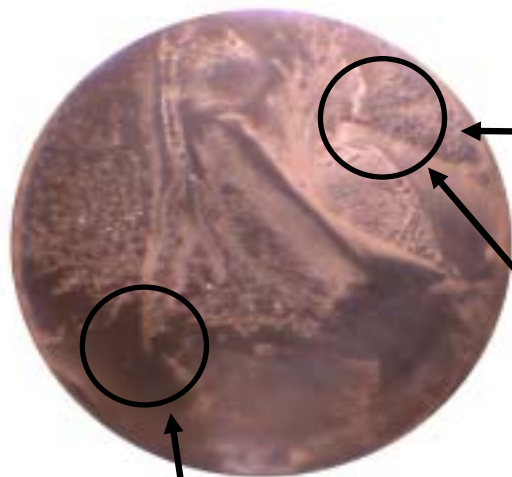- **12.2 L Hydrate View Cell, Environmental Chamber, and Assorted Hardware**
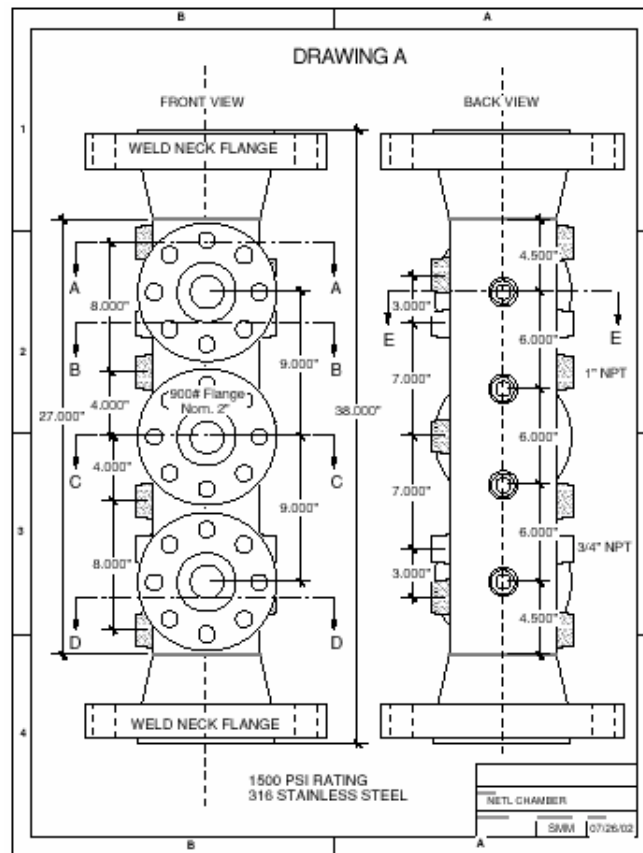
Ultrasonic Probes Measuring Hydrate Formation

Transmitter

Receiver

Solid

Liquid

Raman Spectrometer to Study Hydrates

In Situ Raman Spectra of Methane Hydrate Sample

n=5.81

5 °C

n=18.65

5 °C

n=6.27

5 °C

1400 psig, ~61% methane uptake

In Situ Raman Spectra of Methane Hydrate Sample

n=5.81

5 °C

n=18.65

5 °C
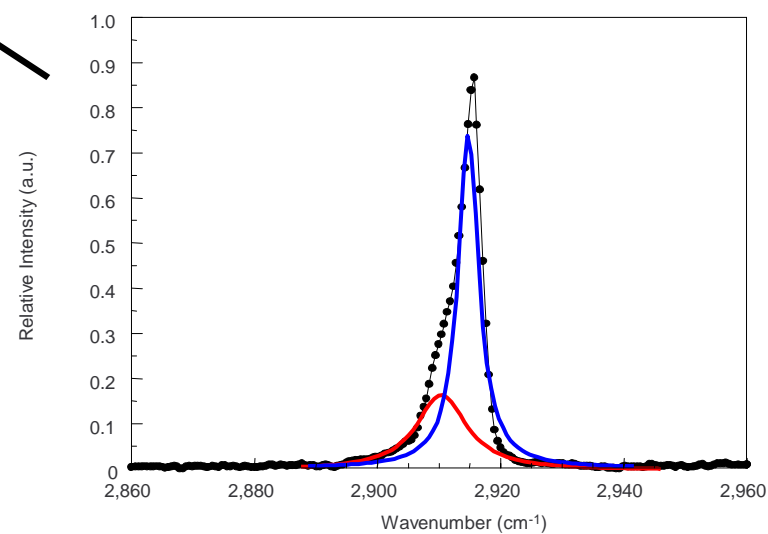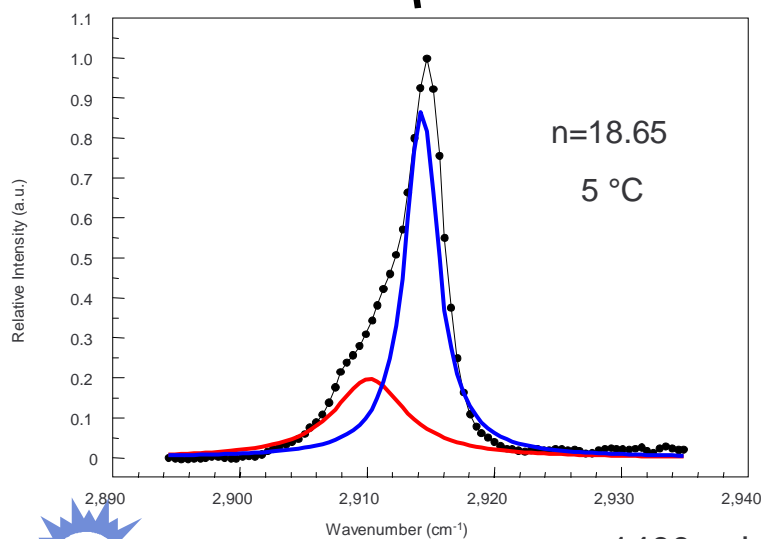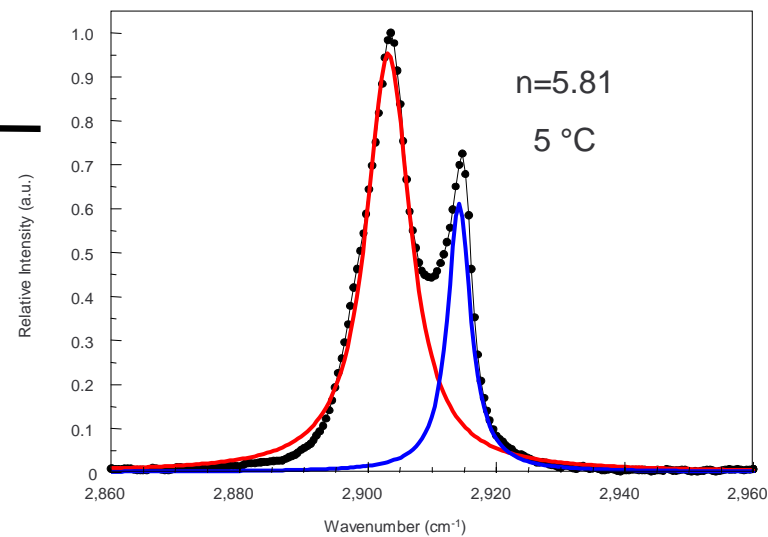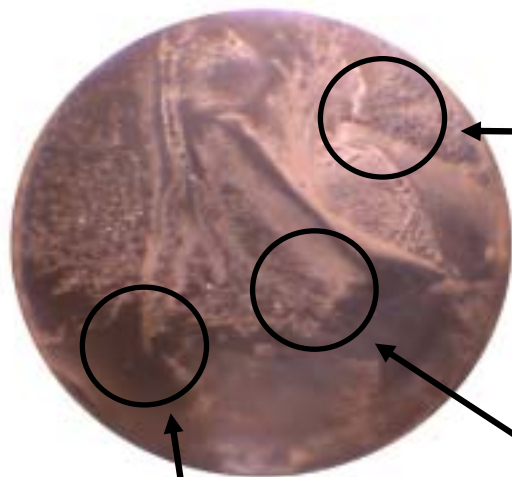
1400 psig, ~61% methane uptake

Conclusions

- **Maximized storage of methane in methane hydrate in binary system occurred under conditions of:**
  - Continuous stirring
  - Constant methane headspace pressure

- **Addition of surfactant approached 99% of theoretical uptake**
  - Sodium dodecylsulfate (SDS) and commercial surfactant showed highest uptake – 97% and 99%, respectively
  - Other surfactants ranged from 15% to 80% uptake

- **Raman studies recently demonstrated that:**
  - Stirring is important to promote homogeneous formation
  - Packing structure can be identified
  - In-lab formations achieve hydration number of ~ 6

Acknowledgements

- **Dr. Christopher Matranga, post-doctoral scientist**

- **Jonathan Lekse, summer student**

- **Oak Ridge Institute for Science Education (ORISE)**